Supplementary Material (ESI) for Chemical Communications

Supplementary materials

Synthesis and Characterization of Rh^{III} Corroles: Unusual Reactivity Patterns Observed During Metallation reactions

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Synthesis. $Rh^{III}(COR)(NEt_2)_2$ 1-3 and $Rh^{III}(COR)$(unhindered base)$_2$. Free base corrole (0.015 mmol) and $[Rh(COD)Cl]_2$ (0.023 mmol) were mixed in dichloromethane(10 ml) followed by addition of the base (0.075 mmol). The mixture was stirred at room temperature until TLC showed complete consumption of the starting corrole. The solvent was then evaporated under reduced pressure. The residue was passed through a column of silica eluting with dichloromethane/hexanes (1:3). The first fraction was collected in 70-90% yield .

$Rh^{III}(TPFC)(NEt_2)_2$ 1. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.15 (d, J = 4.4 Hz, 2H), 8.72 (d, J = 4.8 Hz, 2H), 8.57 (d, J = 4.4 Hz, 2H), 8.49 (d, J = 4.4 Hz, 2H), -2.273 (t, J = 7.2, 12H), -3.22 (m, 4H) -3.41 (m, 4H), -6.06 (b, 2H). UV-vis (CH_2Cl_2), λ_{max} (nm): 446, 412, 590, 658. MS (EI^+) m/z 550.9 (M^+, 100%), 970.1 (15), 1042.2 (18).

$Rh^{III}(TMFC)(NEt_2)_2$ 2. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.20 (d, J = 4.0 Hz, 2H), 9.01 (d, J = 4.8 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.79 (d, J = 4.4 Hz, 2H), 8.24 (dd, J = 8.4, 5.6 Hz, 4H), 8.16 (dd, J = 8.8, 5.4 Hz,, 2H), 7.26 (overlapping dd's, 6H), -2.27 (t, J = 7.2, 12H), -3.22 (m, 4H) -3.23 (m, 4H), -5.82 (b, 2H). UV-vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon \times 10^{-4}$, mol^{-1} L cm^{-1}): 414 (2.3), 442 (3.3), 586 (1.0), 610 (2.0). MS (EI^+) m/z 680.2 (M^+, 100%), 753.4 (20), 828.4 (18).

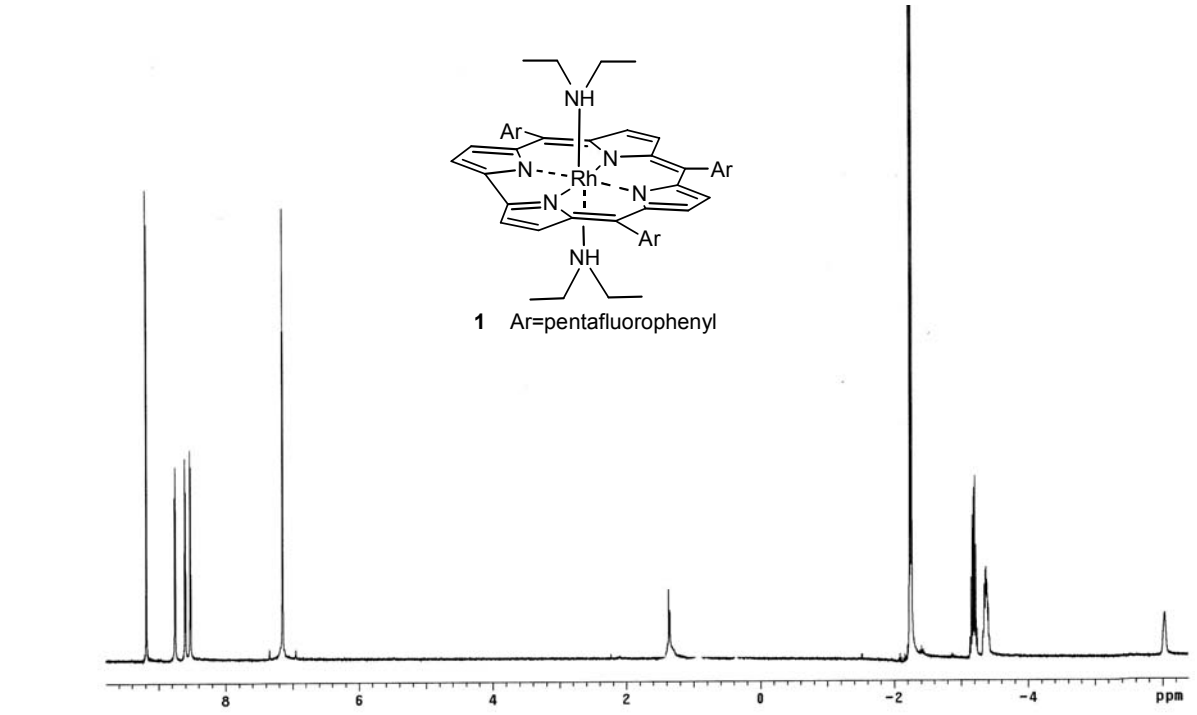
Rh^{III}(BTFC)$(NEt_2)_2$ 3. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.15 (d, J = 4.4 Hz, 2H), 8.96 (b, 4H), 8.80 (b, 2H), 8.79 (d, J = 4.8 Hz, 2H), 8.66 (d, J = 4.4 Hz, 2H), 8.58 (d, J = 4.8 Hz, 2H), 8.22 (b, 1H), 8.20 (b, 2H), -2.46 (t, J = 7.2 Hz, 12H), -3.43 (m, 4H) -3.56 (m, 4H), -6.09 (b, 2H). UV-vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon \times 10^{-4}$, mol^{-1} L cm^{-1}): 434 (11), 570 (2.9). MS (EI^+) m/z 1107.0 (M^+, 100%), 1180.1 (60), 1213.1 (75).

Rh^{III}(TPFC)Py_2. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.10 (d, J = 4.4 Hz, 2H), 8.84 (d, J = 4.8 Hz, 2H), 8.61 (d, J = 4.4 Hz, 2H), 8.57 (d, J = 4.4 Hz, 2H), 4.70 (tt, J = 7.2, 1.6 Hz, 2H), 4.15 (m, 4H), 1.52 (m, 4H). UV-vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon \times 10^{-4}$, mol^{-1} L cm^{-1}): 410 (6.2), 442 (8.4), 552 (1.6), 592 (5.8).

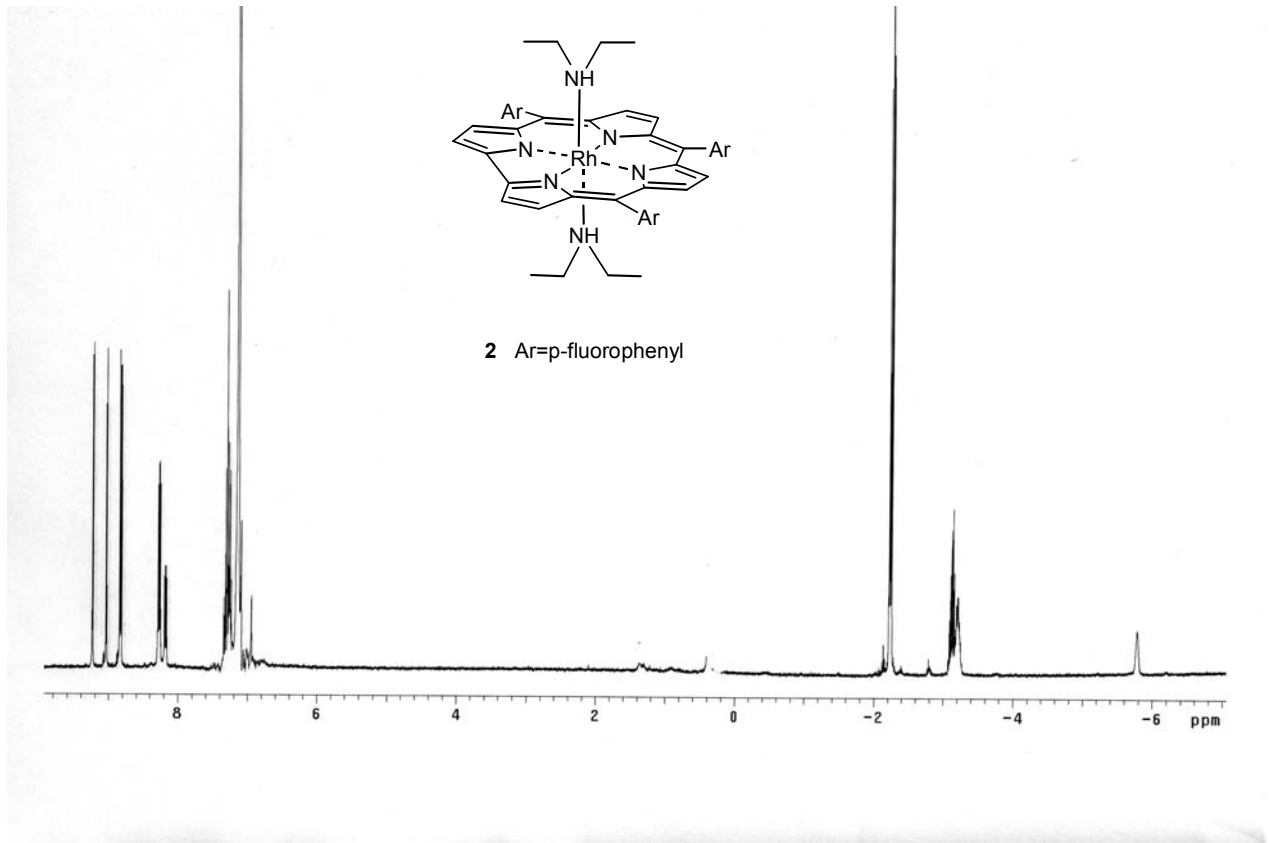
Rh^{III}(TMFC)Py_2. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.24 (d, J = 4.0 Hz, 2H), 9.12 (d, J = 4.8 Hz, 2H), 8.89 (d, J = 4.8 Hz, 2H), 8.88 (d, J = 4.0 Hz, 2H), 8.27 (dd, J = 8.8, 5.6 Hz, 4H), 8.11(dd, J = 8.8, 5.8 Hz, 2H), 7.24 (overlapping dd's, 6H). UV-vis (CH_2Cl_2), λ_{max} (nm) (ε x 10^{-4}, mol^{-1} L cm^{-1}): 414 (2.3), 444 (3.3), 460 (2.6), 586 (1.0), 612 (2.0).

Rh^{III}(BTFC)Py_2. ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.19 (d, J = 4.0 Hz, 2H), 8.92 (b, 4H), 8.86 (d, J = 5.2 Hz, 2H), 8.81 (b, 2H), 8.73 (d, J = 4.0 Hz, 2H), 8.63 (d, J = 5.2 Hz, 2H), 8.16 (b, 1H), 8.14 (b, 2H), 4.64 (tt, J = 7.6, 1.2 Hz, 2H), 3.96 (m, 4H), 1.39 (m, 4H). UV-vis (CH_2Cl_2), λ_{max} (nm) ($\varepsilon \times 10^{-4}$, mol^{-1} L cm^{-1}): 452 (11), 564 (1.3), 610 (5.6). **Rh^{III}(TPFC)$(CH_3$-Py$)_2$ 4-6.** Free base **TPFC** (0.045 mmol) and $[Rh(COD)Cl]_2$ (0.068 mmol) were mixed in MeOH (30 ml) followed by addition of 2,6-lutidine (0.45 mmol). The mixture was stirred at room temperature until TLC showed complete consumption of starting corrole. The solvent was evaporated under reduced pressure. The residue was passed through a column of silica eluting with dichloromethane/hexanes

(1:3). The red fractions were collected as a mixture (65-80% yield). The mixture of three compounds was separated on Alumina plates with 1:9 dichloromethane/hexane as elutes. Fraction 1, **Rh^{III}(TPFC)(4-CH_3-Py)$_2$ 4**, ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.12 (d, J = 4.4 Hz, 2H), 8.89 (d, J = 4.8 Hz, 2H), 8.66 (d, J = 4.8 Hz, 2H), 8.60 (d, J = 4.4 Hz, 2H), 4.00 (d, J = 7.0 Hz, 4H), 1.42 (d, J = 7.0 Hz, 4H), 0.14 (s, 6H). MS (EI^+) m/z 1083.0 (M^+, 100%), 1088.9 (45), 1115.0 (40). Fraction 2, **Rh^{III}(TPFC)(3-CH_3-Py) (4-CH_3-Py) 5,** ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.10 (d, J = 4.0 Hz, 2H), 8.89 (d, J = 4.8 Hz, 2H), 8.64 (d, J = 4.8 Hz, 2H), 8.59 (d, J = 4.4 Hz, 2H), 4.63 (d, J = 7.6 Hz, 1H), 4.21 (dd, J = 7.6, 6.0 Hz, 1H), 4.00 (d, J = 6.8 Hz, 2H), 1.53 (d, J = 6.0 Hz, 1H),1.43 (s, 1H), 1.38 (d, J = 6.4 Hz, 2H), 0.25 (s, 3H), 0.14(s, 3H). MS (EI^+) m/z 896.3 (M^+, 100%), 1081.8 (55), 1082.8 (30). Fraction 3, **Rh^{III}(TPFC)(3-CH_3-Py)$_2$ 6**, ^{1}H NMR (C_6D_6, 400 MHz, δ in ppm): 9.08 (d, J = 4.4 Hz, 2H), 8.89 (d, J = 4.8 Hz, 2H), 8.64 (d, J = 4.8 Hz, 2H), 8.60 (d, J = 4.0 Hz, 2H), 4.61 (d, J = 7.6 Hz, 2H), 4.20 (dd, J = 7.6, 6.0 Hz, 2H), 1.50 (d, J = 5.6 Hz, 2H), 1.40 (s, 2H), 0.24 (s, 3H). MS (EI^+) m/z 1082.0 (M^+, 100%), 1090.0 (35), 1151.1 (15).



1 Ar=pentafluorophenyl



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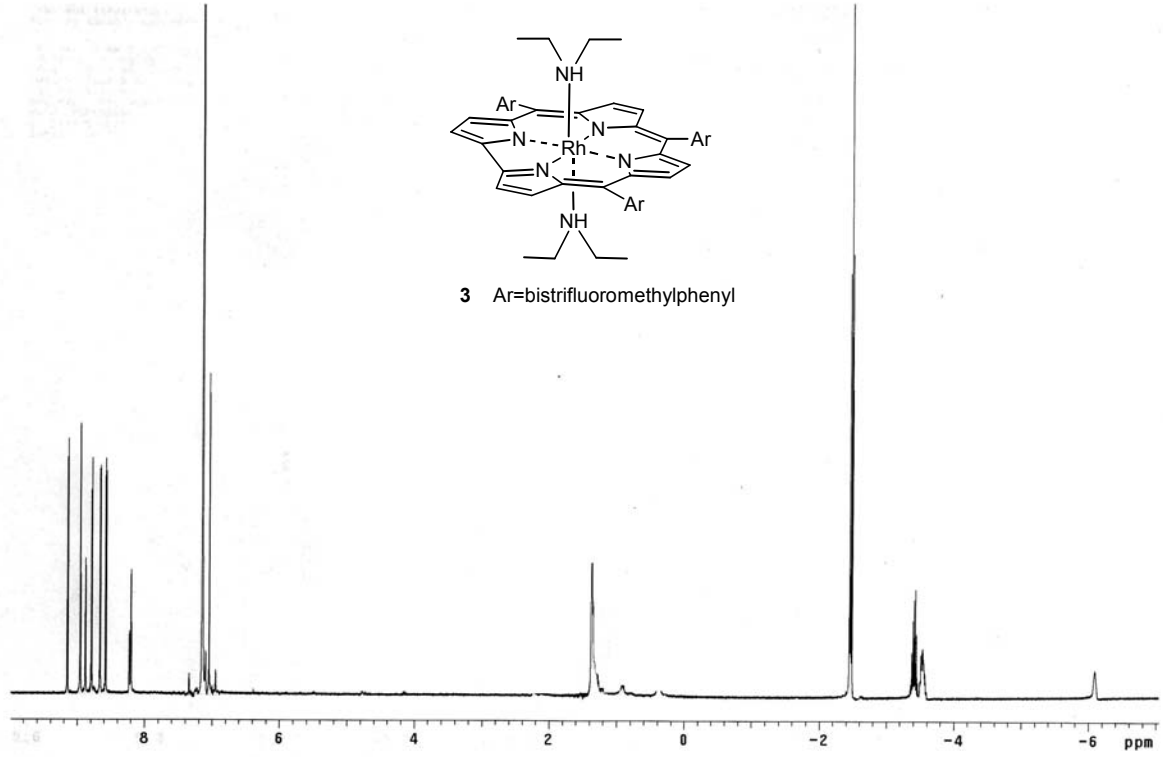
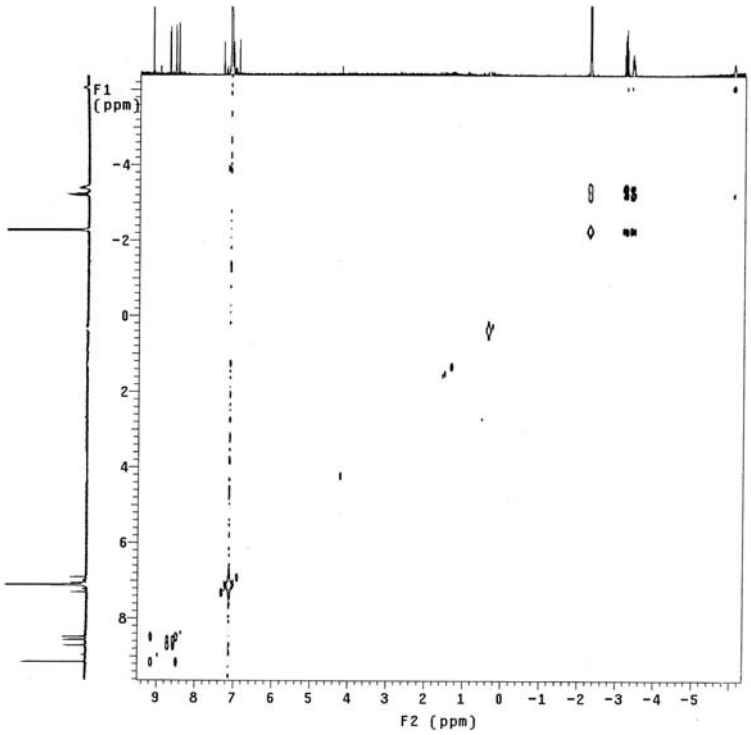
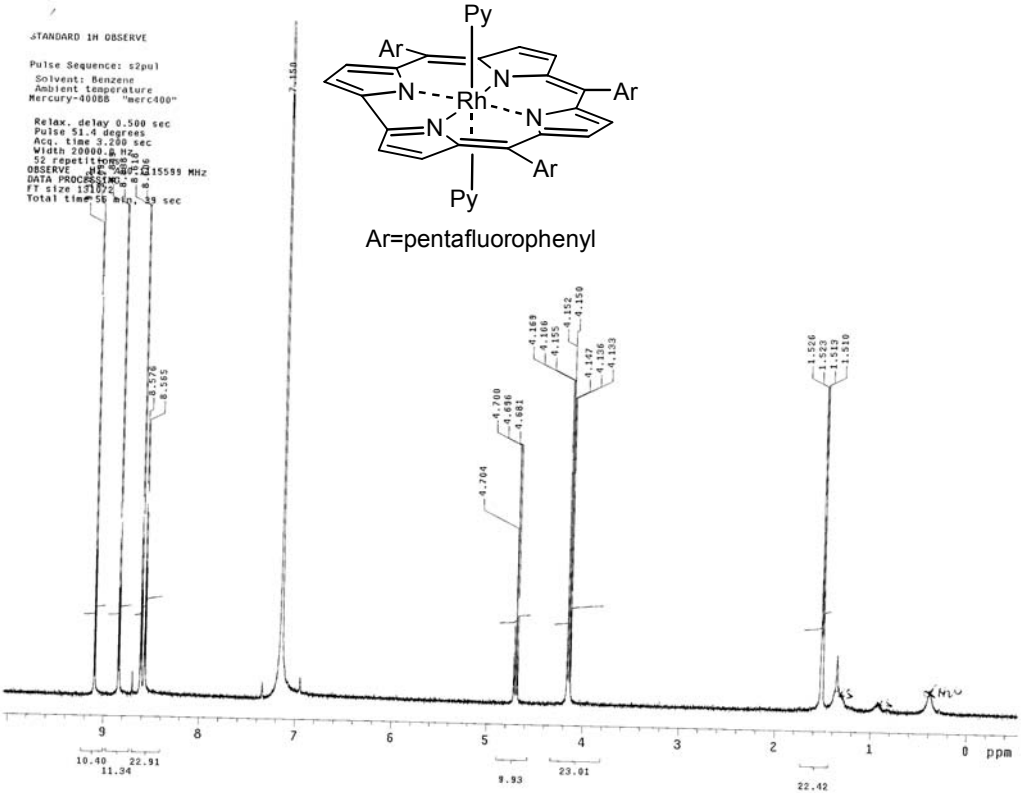
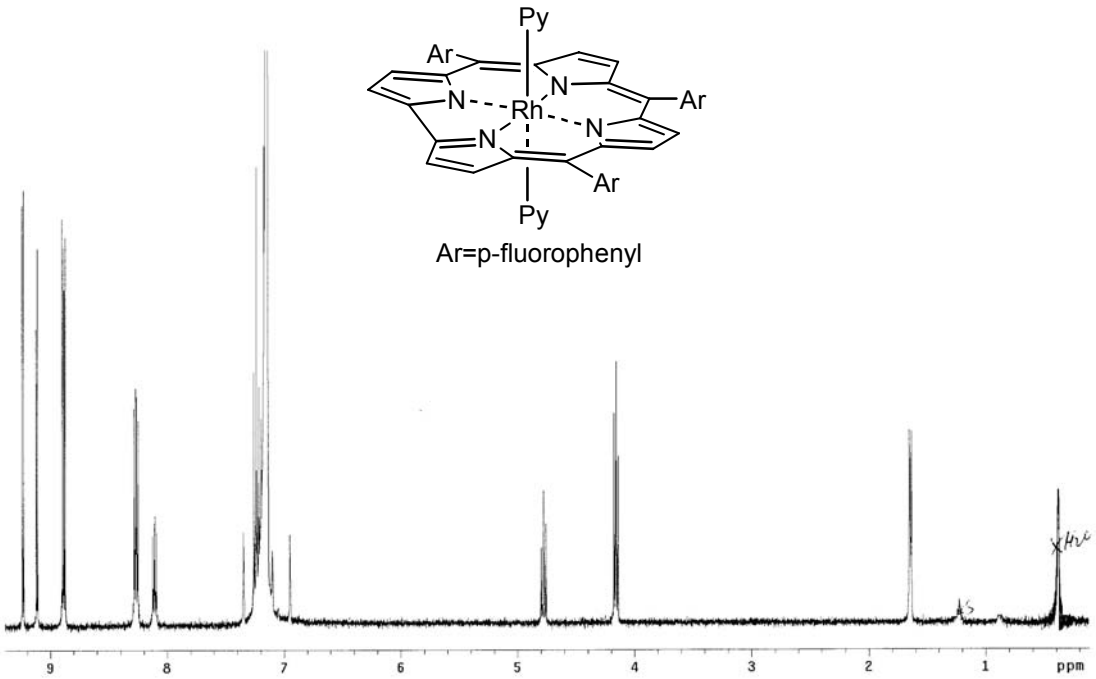


3 Ar=bistrifluoromethylphenyl

^{1}H COSY NMR of compound **1**







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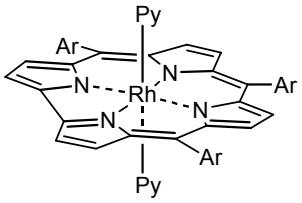

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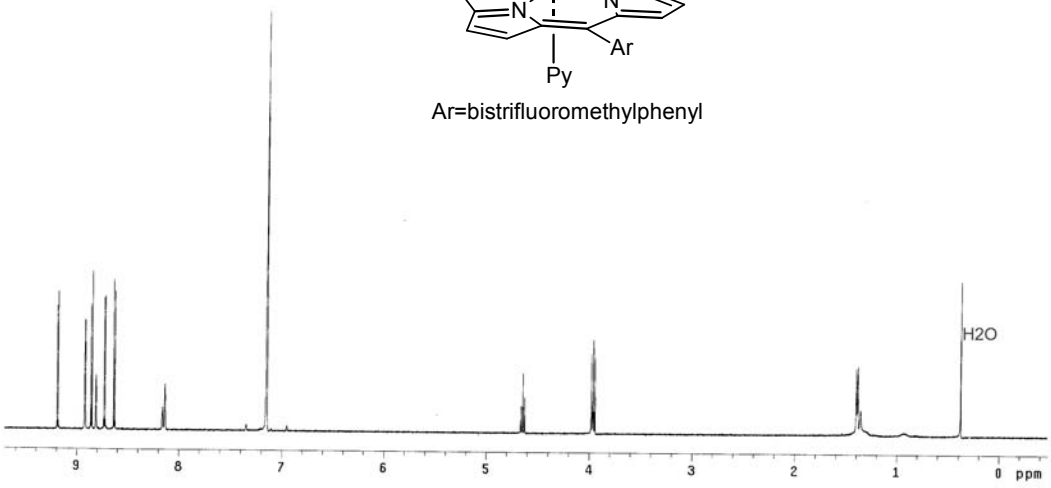
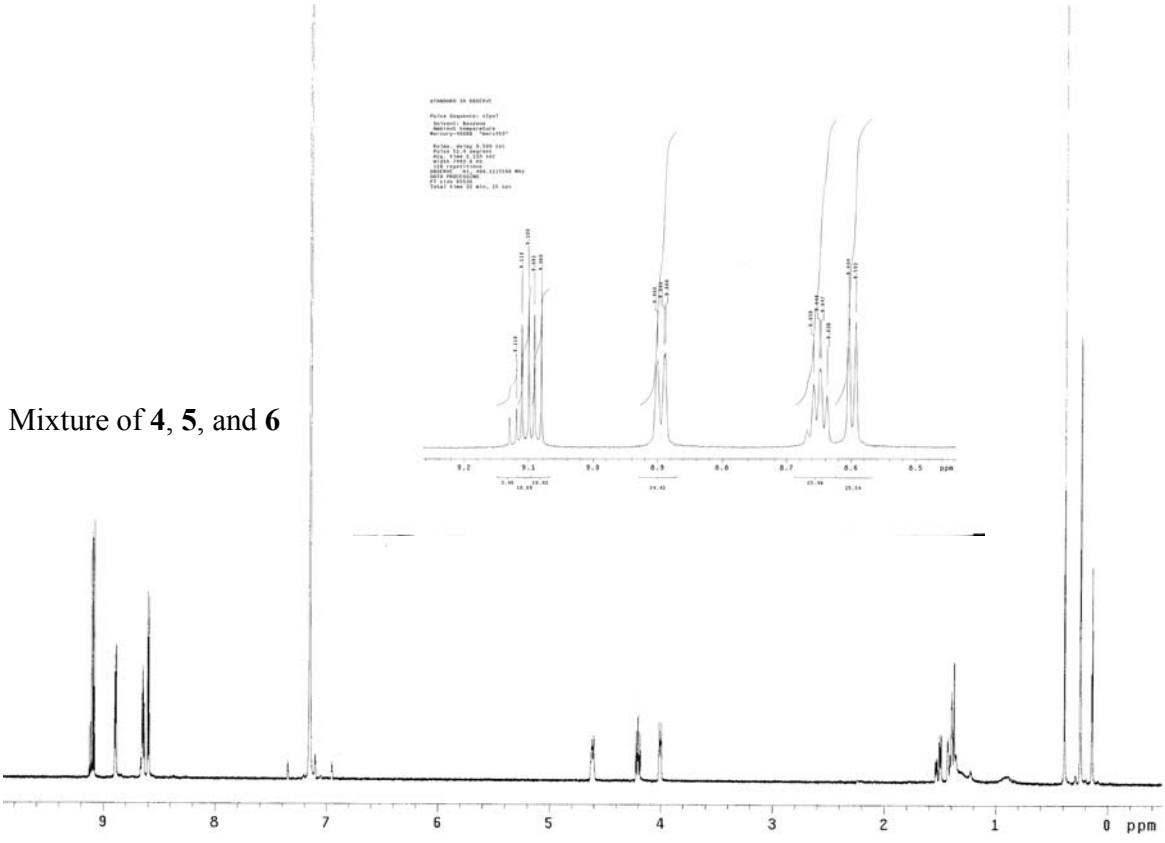
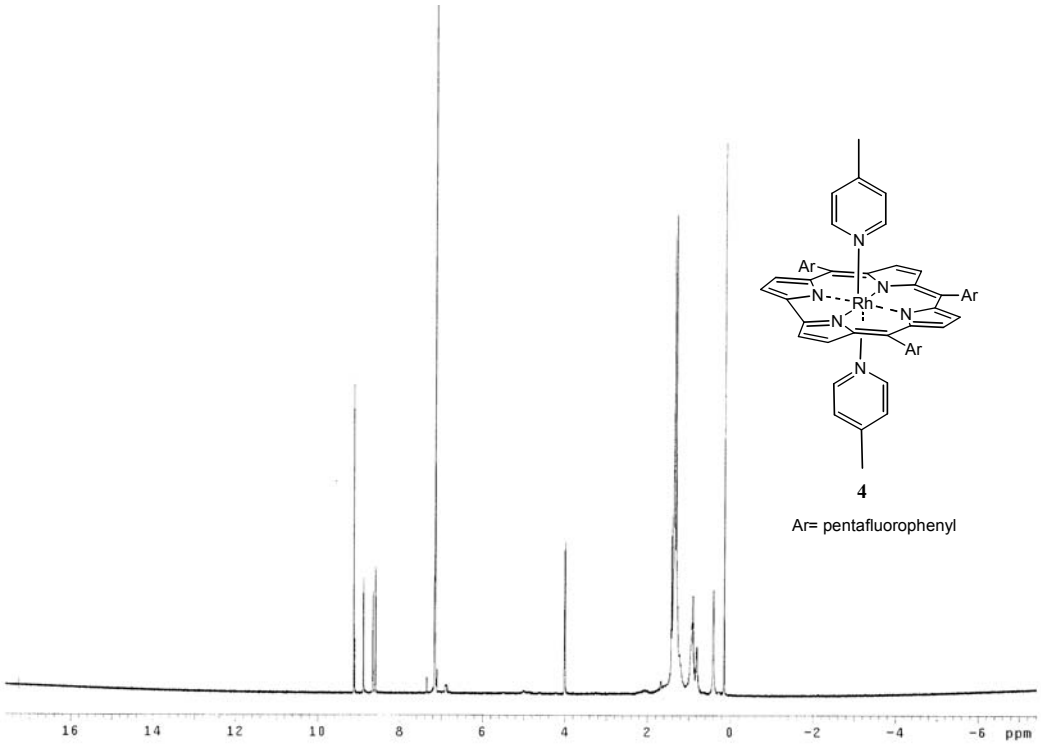


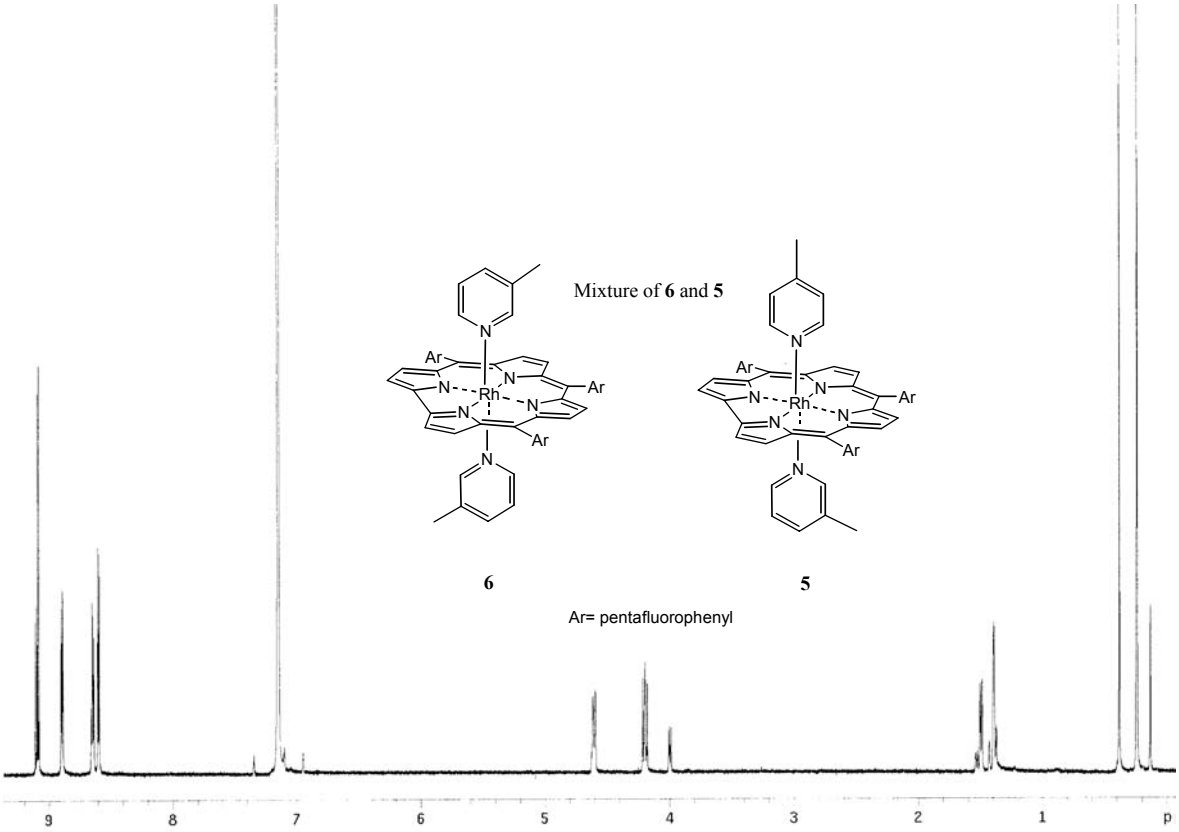
Mixture of **4**, **5**, and **6**





4

Ar= pentafluorophenyl



Mixture of **6** and **5**

6 **5**

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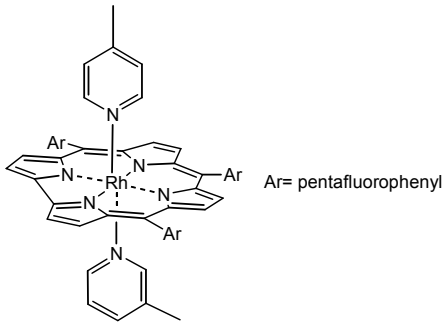
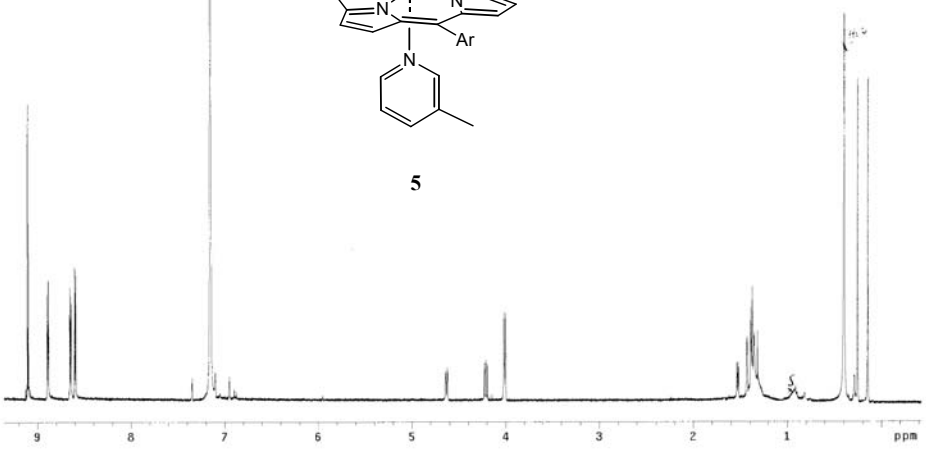
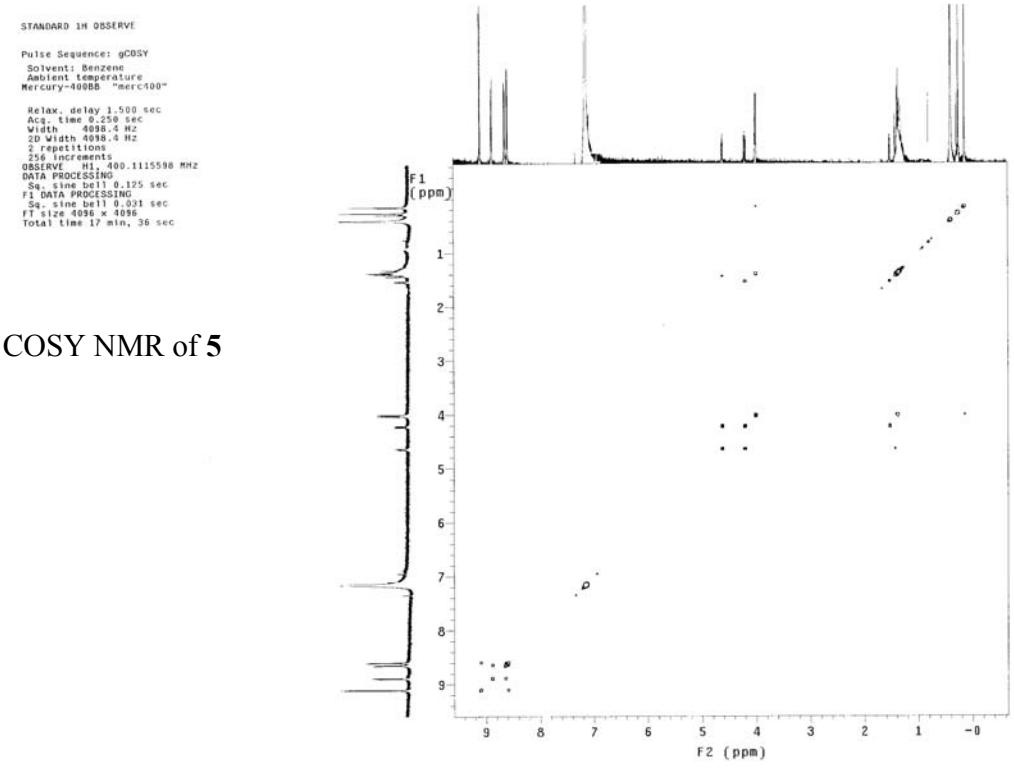


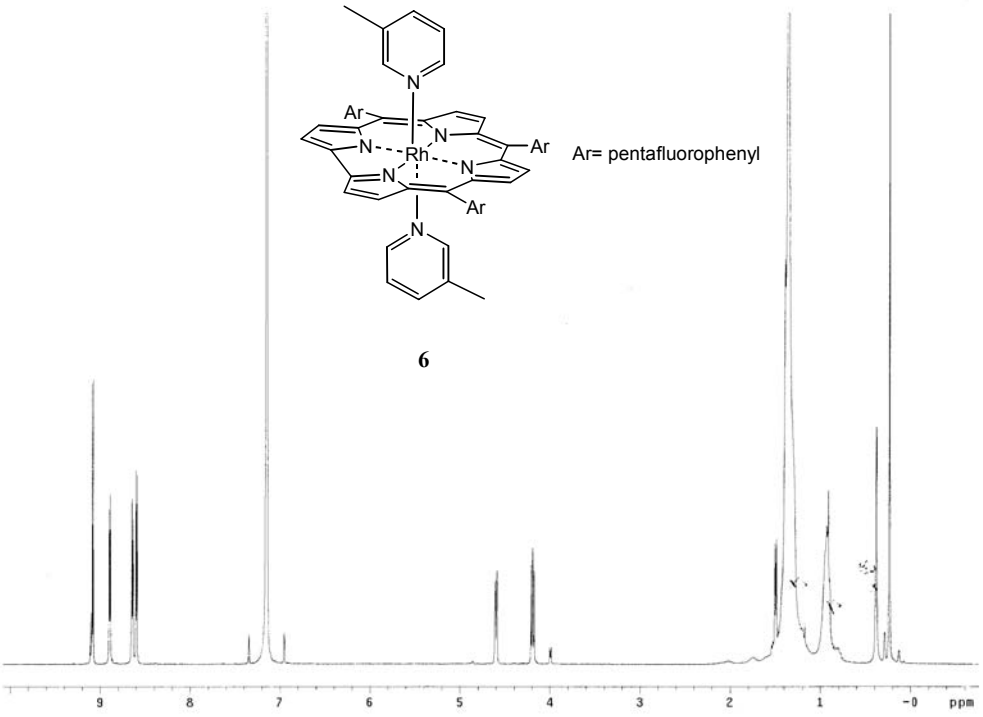
Ar= pentafluorophenyl

5

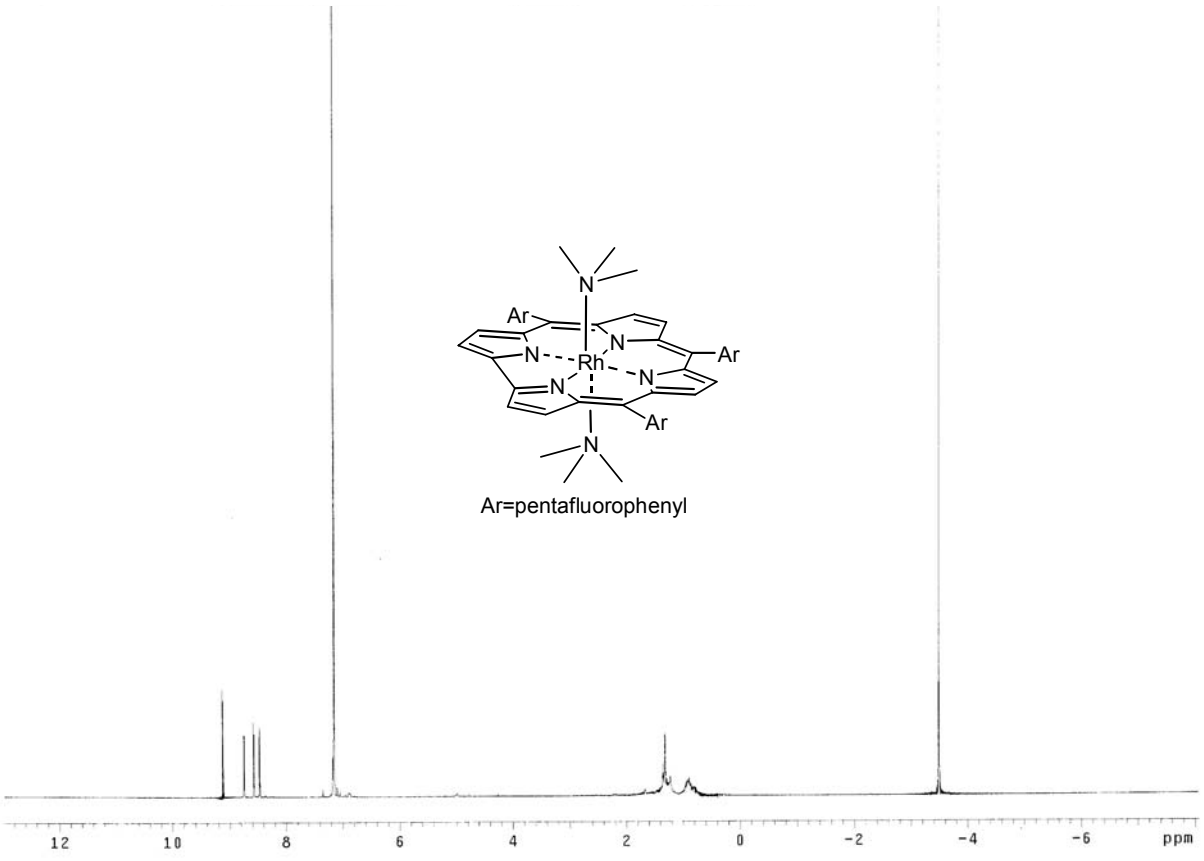


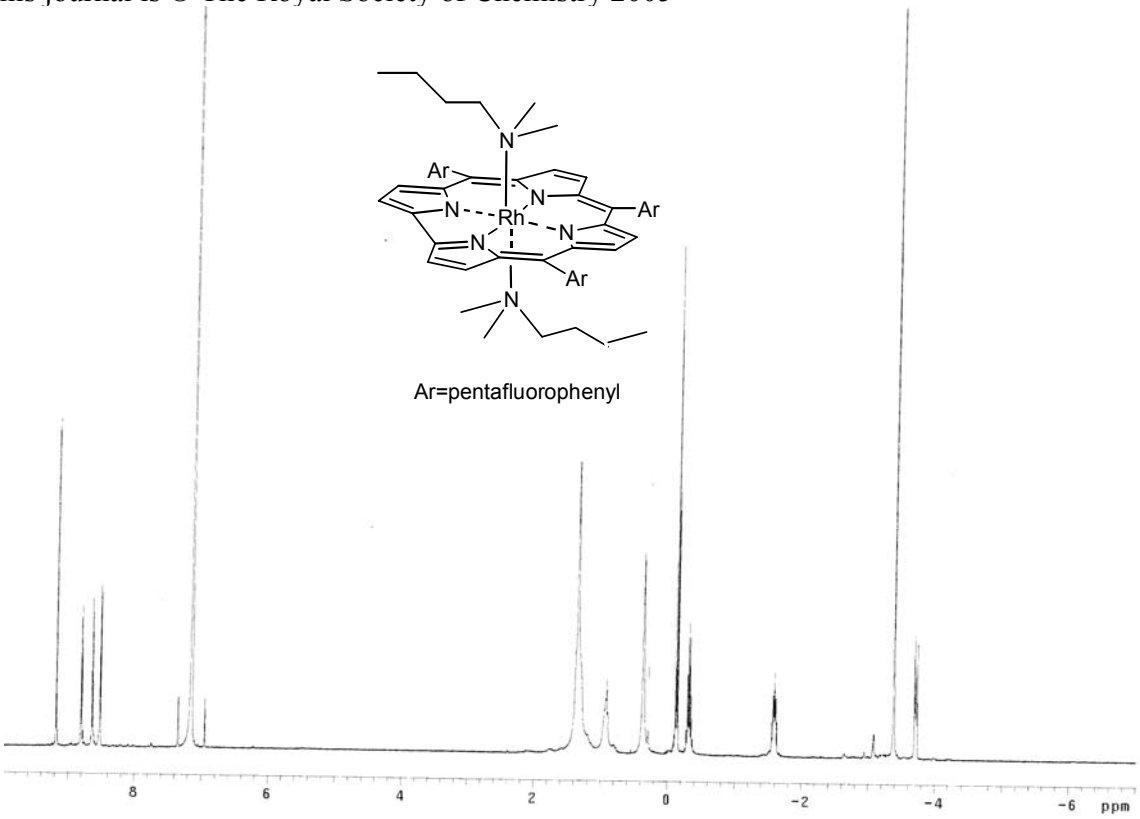


^{1}H COSY NMR of **5**



6





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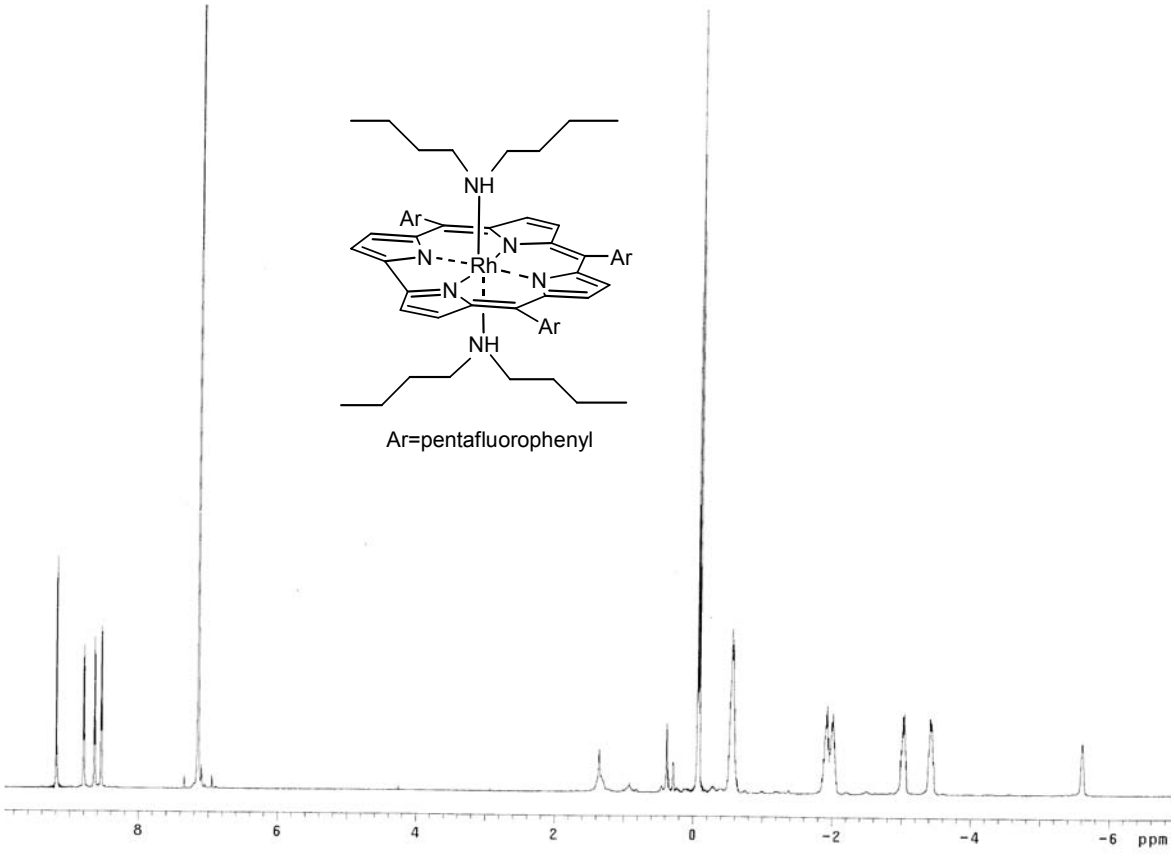

Ar=pentafluorophenyl